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(54) Title: SECURITY PAPER AND SECURITY ARTICLES

(57) Abstract: A security article has at least one security element comprising at least one photoluminescent segment which is characterized by a linearly polarised photoluminescence and/or linearly polarised absorption. A particularly pronounced and well observable effect when embedding such security element in a paper or paper-like structure can be achieved when said paper or paper-like structure is composed of 30 to 99 percent in dry weight fibres and 70 to 1 percent in dry weight filler and optional additives, complementing to 100 percent in total. Preferably, the filler is titanium dioxide or zinc oxide with high scattering and/or absorption properties. According to another preferred embodiment; the paper or paper-like structure is additionally substantially free of brightener and/or additives with fluorescent properties.

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INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference	FOR FURTHER ACTION	see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.
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This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 6 sheets.

[X] It is also accompanied by a copy of each prior art document cited in this report.

1. **Basis of the report**

   a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

   [ ] the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

   b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :

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2. [ ] **Certain claims were found unsearchable** (See Box I).
3. [X] **Unity of invention is lacking** (see Box II).

4. With regard to the **title,**

   [ ] the text is approved as submitted by the applicant.
   [X] the text has been established by this Authority to read as follows:

   SECURITY PAPER AND SECURITY ARTICLES

5. With regard to the **abstract,**

   [ ] the text is approved as submitted by the applicant.
   [X] the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No. ______

   [ ] *as suggested by the applicant.*
   [ ] because the applicant failed to suggest a figure.
   [ ] *because this figure better characterizes the invention.*
   [X] *None of the figures.*

DESCRIPTION

TITLE

Security paper and other security articles

FIELD OF THE INVENTION

The present invention relates to security paper and security articles in general, the forgery of which shall be hampered or rendered impossible through one or more security elements. In particular the present invention relates to security articles characterised by at least one security element comprising at least one photoluminescent segment which is characterised by a linearly polarised photoluminescence and/or linearly polarised absorption. The present invention also relates to a method to produce such security articles and a method to use the latter.

BACKGROUND OF THE INVENTION

It is commonly known that for security papers and security articles in general, for example for banknotes, checks, stocks, bonds, identification cards, passports, drivers licenses, tickets, stamps and similar documents such as bank cards, credit cards, and the like, security elements can be employed, which have the purpose to prevent or stifle forgery of those objects by unauthorised persons (R. van Renesse "Optical Document Security" (1997), Artech House, Boston). Such security elements are also used to mark the authenticity or validity of object, or generally to enable or facilitate the identification of objects. It is, for example, widely known to use security threads or security strips which can consist of, among other things, a metal coated polymer, in security paper, especially for the application in banknotes and similar documents. When such security threads or strips are, for example, embedded in the security paper and the paper is subsequently printed, the thread or strips cannot be readily discerned in reflective light but immediately appear as a dark image when the document is viewed in transmitted light.

In order to ensure and enhance the security of security articles against modern counterfeiting techniques, in recent times it was repeatedly proposed to provide the security elements with specific properties, such that not the mere presence of the security

element alone, but the presence of its specific properties shall guarantee the authenticity of the secured object (US 4,897,300; US 5,118,349; US 5,314,739; US 5,388,862; US 5,465,301, DE-A 1,446,851; GB 1,095,286). For example, DE-A 1,446,851 describes a security thread having a microprint executed in multiple colours; the printing ink used can also be fluorescent. The areas printed with different colours are so small or so close together that they cannot be distinguished by the naked eye and, therefore, appear to the viewer as one uniform colour. The microprint or the different colours can only be recognised with the aid of a magnifying glass or a microscope. A similar security element is disclosed in GB 1,095,286 where the microprinted areas are letters or patterns. Another security paper is described in US 4,897,300. Here, multiple security threads which are printed with different luminescent dyes are embedded in the security paper. The latter are colourless or have the colour of the paper and are, therefore, not or only hardly visible to the viewer. When excited, however, for example through irradiation with ultraviolet (UV) light, the security threads luminesce. According to US 4,897,300, the latter have a size that allows the detection with the naked eye. Through the overlap of security threads of different colour, characteristic, mixed colours can be achieved. In order to further enhance the security of security papers, in particular banknotes, it is common to integrate a security thread or strip into the paper such that "windows" in the paper surface allow a direct view on parts of the surface of the security element as, for example, disclosed in GB 1,552,853, GB 1,604,463 or EP 0,059,056.

However, it is generally considered a grave disadvantage of all these known security elements that either the characteristic authenticity marks are rather difficult to recognise for a laymen, or that complex instruments have to be used for their detection. On the other hand, security elements which can easily be recognised can usually relatively easily be forged. Furthermore, it is in the nature of security articles that they are replaced by novel products with novel security elements after a comparably short time; in particular with the purpose to stifle forgery and abuse. Therefore an urgent need exists for novel, security elements of high security which are easily recognised, for applications in security paper and security articles in general. For example WO 00/19016 describes such novel security elements based on their dichroic properties. The document describes security elements or segments incorporated into a paper or the like, which security elements show either linearly polarised photoluminescence or linearly polarised absorption. These security elements provide security paper and security articles in general which are characterised by secure, easily recognisable security elements. The document additionally describes security paper and security articles in general, the identification of which is enabled or facilitated through such security elements and it also describes the development of methods for the production of these security articles and the use of the latter.

However, problems arise when trying to incorporate the security elements into paper, as on the one hand the elements have the tendency not to be sufficiently fixed within the

paper matrix and the polarisation efficiency (absorption as well as emission) is reduced when these elements are incorporated in the paper.

SUMMARY OF THE INVENTION

To start with, some of the most important terms shall be defined:

Definitions:

The term security element relates to a, for example, shaped object that can have a variety of shapes, for example, but not only, fibre, thread, rod, tape, film, windows and/or combinations thereof. The security element can be homogeneous and continuous and can be structured or patterned and can comprise multiple individual elements, zones or pixels.

The term security article relates to objects, the forgery of which shall be hampered or rendered impossible through one or more security elements, or the authenticity or validity of which shall be marked through one or more security elements, which shall be identified by one or more security elements; for example, but not limited to banknotes, checks, stocks, bonds, identification cards, passports, drivers licenses, tickets, stamps, bank cards, credit cards. The term security article shall include woven such as textiles and non-woven articles such as paper or foil.

The term security paper relates to security articles which substantially are made from paper. It particularly but not exclusively relates to non-woven, flat, fibre-containing data carriers.

In order to describe the operation and properties of segments, security elements, security articles, and the conditions of experiments, the following common definitions of the several axes will be used:

The polar axis of a linear polarizer or analyzer is the direction of the electrical field vector of the light that is transmitted by the polarizer films. The polar axis of a segment or - if applicable - security element or other object is the direction of the electrical field vector of the light that is emitted or absorbed by the respective segment, security element, or other object.

The term segment is used for a part of an object, in particular of a security element, for which the characteristic degree of polarization and polar axis for absorption and emission can be determined in appropriate manner.

The degree of emission polarization (also referred to as degree of polarization in emission) is expressed as the emission dichroic ratio (also referred to as dichroic ratio in emission). The emission dichroic ratio is defined as the ratio of the integrated emission spectra measured through a linear polarizer (analyzer) with its polar axis parallel and perpendicular to the polar axis of the investigated segment, using unpolarized excitation light.

The degree of absorption polarization (also referred to as degree of polarization in absorption) is expressed as the absorption dichroic ratio (also referred to as dichroic ratio in absorption). The absorption dichroic ratio is defined as the ratio of the absorption measured with incident light linearly polarised parallel and perpendicular to the polar axis of the investigated segment, and is measured at the wavelength used for excitation.

The excitation wavelength is defined as the wavelength that is used for optical excitation (to generate photoluminescence) of the security element or its photoluminescent segments, respectively. The terms absorption and emission relate to optical processes.

It is the object of the present invention to overcome the problems of the prior art security articles. In particular in the context of security articles characterised by at least one security element comprising at least one photoluminescent segment which is characterised by a linearly polarised photoluminescence and/or linearly polarised absorption, well visible and easily detectable effects due to embedded photoluminescent segments shall be achieved.

This object is achieved by the technical features given in the characterising portion of the main claim. More particularly, the object is achieved by embedding the photoluminescent segment in a paper or paper-like structure composed of 30 to 99 percent in dry weight paper-fibres and 70 to 1 percent in dry weight filler and optionally further additives, complementing to 100 percent in total. Such additives may be the ones conventionally used for paper like e.g. binder, resin, surfactants, colorants, antifoaming agent, and additives to e.g. provide desired surface/printing properties etc.

It is found that usually problems arise when embedding security elements into paper or paper-like structures due to the fact that security elements which are partially or fully buried under a layer of paper or paper-like matrix, do not show the expected linearly polarised photoluminescence and/or linearly polarised absorption anymore to the extent as observed for the separate security element. Surprisingly however, this problem can be largely overcome when the content in paper-fibres is adjusted within the range given in the characterising portion. Due to the structural orientation and due to the associated inherent fluorescent properties of paper fibres, and/or rather due to residual substances present in conventional paper fibres like lignines, resins, abietic acids etc., the desired effect of the security elements embedded within such paper-fibres is disturbed.

According to a preferred embodiment of the present invention, the paper or paper-like structure is additionally substantially free of brightener and/or additives which itself have fluorescent properties in particular which itself show linearly polarised photoluminescence and/or linearly polarised absorption. In other words, such substances should not be excessively present in the matrix. There is quite a large number of additives commonly used in the production of paper which comprise chromophores with fluorescent properties when irradiated with ultraviolet irradiation. There are for example binders with particular resins exhibiting such properties detrimental to the present application. Additionally, many

of the brighteners commonly used in the production of paper or paper-like structures are based on dyes which comprise chromophores which themselves have fluorescent properties. These additionally hamper the efficiency of the security elements. One particular class of brighteners commonly used are stilbene-based brighteners which have pronounced fluorescent properties, and therefore these brighteners should not be present to the extend that they interfere with the desired security feature. If such substances are present in the matrix of the security article, this matrix exhibits a very bright appearance when irradiated with ultraviolet irradiation leading to a low contrast between the matrix and the security elements. Additionally, transfer between these fluorescent chromophores and the security elements may lead to a destruction of the polarisation efficiency as macroscopically detectable when e.g. looking at the irradiated security elements e.g. through a rotating polarization filter or observing the security elements in linearly polarised light.

According to another preferred embodiment of the present invention, the security article is characterised in that the filler has high scattering properties and/or high absorption properties in the spectral range used in particular for irradiation and/or also for detection. To enhance the particular macroscopically detectable polarisation effects (by enhancing the contrast of security element and matrix) or rather not to disturb the polarising effects due to the security elements, the filler should be chosen such as to absorb as much of the incident polarised or not polarised radiation as possible. Among the various species useful for this purpose, in particular, titanium dioxide in its rutile and/or in its anatase modification proves to be of use as well as zinc oxides. A particularly pronounced beneficial effect is achieved when employing titanium dioxide in its rutile-modification. Already amounts in the range of 0.5 to 5%, preferably 1 to 2% w/w of rutile may suffice to achieve the desired effect even when other fillers which do not have these absorption properties are at the same time present. Usually less than 5% w/w suffice. It has to be noted however, that if for example additives or brightener are present in the matrix of the security article which have fluorescent properties, a larger amount of filler with the above-mentioned absorbing properties may be necessary. When e.g. rutile is used as filler (at least in a fraction as mentioned above), the paper-like structure appears completely dark when irradiated with ultraviolet irradiation which means that the incident light is completely absorbed by this filler. Also anatase and zinc oxide filler show this effect, but to a slightly lesser degree. This leads to two effects which are particularly advantageous in the present context:

1. almost no incident light reaches security elements which are buried under a (thin) layer of paper-matrix thus avoiding that these buried elements are irradiated by light which is not highly polarised in case of polarised excitation. When polarised light is used for polarised excitation, this polarisation is partially or fully lost when this light passes through layers of the matrix carrying the security element. Correspondingly, light emitted by buried security elements is also not highly polarised anymore leading to a masking of the desired bright/dark effect when for

example rotating the polarisation axis of the incident light. The same is of course true if the incident light is not polarised but if detection is carried out using a polarisation filter (linearly polarised photoluminescence). In this case the photoluminescence emitted by the security elements which are buried is also reduced in its polarisation when passing through the layer covering the buried security element leading to a masking or even to a loss of the bright/dark effect. Surprisingly, it has been observed, that if rutile (or another filler, organic or inorganic, having these properties, namely to be isotropically absorbing the irradiated light on a macroscopic scale) is being at least partially present in the filler, this effect can be reduced or avoided. This is due to the high scattering effects of the rutile particles and/or due to the absorption properties of these particles. The particularly high refractive index of rutile (which is higher than e.g. for the anatas-modification of titanium dioxide) is quite well known. However, that this leads to the advantageous effects in the context of the present application of embedding security elements is surprising finding. Even more so as the particle size of the titanium dioxide in rutile-modification does not seem to have a determining influence in this question. The highly symmetric structure of the unit cell of the rutile structure leads to fully isotropic properties when polarised light is irradiated, which in fact also seems to have influence in the present context.

2. Another advantage of using rutile or another functionally similar substance at least partially as filler is due to the black appearance of the paper-like structure when irradiated with light thus increasing the contrast between the paper matrix and the bright/dark appearance of the security elements.

According to another preferred embodiment of the present invention, the paper-fibres at least partially comprise synthetic-fibres like for example polypropylene-fibres, polyethylene-fibres, aramide-fibres, polyacrylonitrile-fibres and/or at least partially comprise natural raw material based fibres selected from the group of wood-fibres, cotton-fibres, grass-fibres, cellulose-fibres, viscose-fibres, lyocell-fibres, rayon-fibres.

According to a further preferred embodiment of the present invention, at least one of the security segments characterised by linearly polarised absorption. In particular in relation with the application in the field of detection of false banknotes, irradiation with e.g. ultraviolet light of rotating polarisation (for example provided by an ultraviolet lamp which is covered by a rotating polarisation filter) the bright/dark effect can be observed very easily while using as little instrumentation as possible.

According to a further preferred embodiment of the present invention, the security segment is characterised by a dichroic ratio of 2 or more in absorption and/or emission, preferably of 5 or more in absorption and/or emission, and even more preferably by dichroic ratio of 10 or more in absorption and/or emission. In particular in the field of security elements for banknotes dichroic ratios of more than 5 are useful. The security segments may have various shapes such as fibres, threads, rods, tapes, films, windows,

or a combinations thereof, and may be either be homogeneously distributed within the paper or paper-like matrix or may also be provided in particular arrangements to further beneficially enhance the bright/dark effect. Also possible are stripes extending substantially across the entire security article.

In another preferred embodiment, the security segment can be excited to photoluminesce through exposure to electromagnetic irradiation of a wavelength between 200 and 500 nm. Ultraviolet irradiation is particularly useful as sources for providing such light are quite cheap and may be used without any human noticing it unless some of these particular security elements with particular dyes are being brought near such light.

There are different carrier materials which are particularly suitable for forming said security segments. The carrier material carrying the photoactive dye must allow an incorporation of the dye leading to a macroscopic polarisation effect. Usually that requires that the carrier allows an oriented incorporation/embedding of the dye which means that it should usually have some structural orientational order which may be achieved by stretching for example. For crystalline species, this high orientational order is measurable e.g. by wide-angle x-ray diffraction, where the order should be characteriseable by a half width at half height of less than 25 degrees, preferably of less than 15 degrees, and even more preferably of less than 10 degrees. Another possible mechanism allowing for oriented adsorption of the dye on the surface of the security carrier may be a particularly orientationally structured surface of said carrier, for example through graphoepitaxy. On the one hand the security segments may be made of a polymer carrier, preferably polyethylene, polypropylene, polycarbonate, polyester, polyamide, polyacrylonitrile, polyvinyl alcohol, aramide, or other materials e.g. used in the field of textile fibres, or mixtures thereof, dyed with a photoluminescent dye. On the other hand said security segments may be made of a cellulose-based carrier dyed with a photoluminescent dye. This carrier is of particular advantage as fibres or other security elements made of such carrier provide surface properties allowing for firm and easy embedding into a common, cellulose-based paper matrix. Cellulose-based elements shows the same behaviour with respect to hydrogen bonding as the material being used for the paper matrix, thus ensuring tight attachment to this particular paper matrix. Especially, such security segment may be made of viscose, or lyocell. The elements may e.g. be in the form of fibres with a length of 0.5 to 25 mm, preferably of 1.0 to 10 mm at 1 to 50 dtex, preferably at 5 to 20 dtex, which fibres may be incorporated/embedded into a paper matrix. Also possible are security elements in the form of threads/stripes extending over substantially the entire security article with a width in the range of 0.5 to 20 mm and a thickness of in the range of 5 μm to 100 μm. Further generally possible are textile fibres with more than 1 dtex. Particularly well suited due to their high degree of orientation and due to their ease with respect or dying are lyocell-fibres as obtained by the NMMO-process, such as those manufactured by for example Lenzing. Particularly distinct effects can be achieved if the fibres are as little distorted as possible and show as little fibrillation as possible. A high transparency of the fibres is of advantage as well.

The security elements may also be patterned or otherwise modified after the dying/stretching process, for example to destroy the polarisation effect in certain regions. This may be achieved by methods like local heating such that the structural order in the heated region gets lost due to melting leading to isotropic distribution of dye in these regions(so called embossing). Another possibility is to irradiate selected regions of the dyed security elements with high-energy (ultraviolet) irradiation leading to destruction of the chromophores and subsequent bleaching of the irradiated regions. Both methods allow the design of particular forms, stripes, characters, logos, etc. on the security elements adding to the securing effect of such elements.

According to still another preferred embodiment of the present invention, the paper or paper-like structure is composed of 80 to 97 percent in dry weight fibres and 20 to 3 percent in dry weight filler and optionally additives, complementing to 100 percent in total.

Further preferred embodiments of the security article according to the present invention are described in the depending claims.

The present invention additionally concerns the application of a security article as described above for objects the forgery of which shall be made difficult or impossible, for objects the authenticity and/or validity of which shall be marked, for objects the identification of which shall be enabled and/or facilitated and/or for an object selected from the group consisting of banknotes, checks, stocks, bonds, identification cards, passports, drivers licenses, tickets, stamps, bank cards and credit cards.

Furthermore, the present invention also concerns processes for the production of security articles, characterised in that at least one security segment is dyed with a photoluminescent dye prior or after its structural orientation, and is then embedded in a paper-like matrix. As mentioned above, the security element/segment may subsequently also be treated in certain regions to selectively modify or erase the polarisation effect in these regions.

Concerning the embedding/incorporation of security elements in the paper-like matrix, this may be achieved by using conventional paper-making techniques. It is, however, also possible to introduce the security elements only in certain layers, preferentially in the surface layers of the security article (e.g. multi-layer paper or data carrier) to prevent that a large number of security elements is buried within the security article without substantially giving rise to the desired polarisation effects. Such a multi-layer paper may for example be produced by laminating 2 flow boxes immediately behind the 2 vats/cylinders, where only one of them comprises polarising fibres. It may additionally be possible to incorporate fibres in a particular coating covering a security article.

DETAILED DESCRIPTION OF THE PRESENT INVENTION

The present invention is based on our finding that photoluminescent materials which are characterised by linearly polarised photoluminescence or linearly polarised absorption or

both and can be made in a form according to the present invention, can be employed to produce security elements that can be used for the production of security paper and security articles in general. Most importantly, we found the security paper and other security articles according to the present invention are characterised by a high security against counterfeiting and are characterised by authenticity marks that can easily be recognised. However, problems arise when embedding the security elements into paper or some other security article due to the fact that this matrix may reduce or disturb the efficiency of the photoluminescence effects that can be observed.

The general fact that certain luminescent materials can exhibit linearly polarised absorption and emission has been known for long times; these effects have first been observed in inorganic crystals (E. Lommel, Ann. d. Physik und Chemie, Vol. 8, pp. 634-640 (1879)) and later in oriented blends of ductile polymers and low-molecular weight luminescent materials (A. Jablonski, Acta Phys. Polon., Vol. A 14, pp. 421-434 (1934)). Since, a number of materials has been described that exhibit linearly polarised absorption and emission (J. Michl et al. "Spectroscopy with polarised light" (1986), VCH Publishers, New York) including, for example, oriented blends of ductile polymers and oligomeric photoluminescent materials with significant uniaxial component (M. Hennecke et al., Macromolecules, Vol. 26, pp. 3411-3418 (1993)), oriented photoluminescent polymers (P. Dyreklev et al., Adv. Mater., Vol. 7, pp. 43-45 (1995)) or blends thereof and a ductile polymer (US Patent 5,204,038; T. W. Hagler et al., Polymer Comm., Vol. 32, pp. 339-342 (1991); Ch. Weder et al., Adv. Mater., Vol. 9, pp. 1035-1039 (1997)), liquid crystalline systems (N. S. Sariciftci et al., Adv. Mater., Vol. 8, p. 651 (1996); G. Lüssem et al., Adv. Mater., Vol. 7, p. 923 (1995)) or oriented photoluminescent materials grown onto orienting substrates (K. Pichler et al., Synth. Met., Vol. 55-57, p. 454 (1993); N. Tanigaki et al., Mol. Cryst. Liq. Cryst., Vol. 267, p. 335 (1995); G. Lüssem et al., Liq. Cryst., Vol. 21, p. 903 (1996); R. Gill et al., Adv. Mater. Vol. 9, pp. 331-334 (1997)). Also recently materials have been described that are characterised by an essentially unpolarized absorption but a linearly polarised emission (C. Weder et al., Nature, Vol. 392, p. 261; European Patent Application 98101520.9). Similarly materials can be obtained that are characterised by an essentially unpolarized emission but a linearly polarised absorption (European Patent Application 97111229.7; European Patent Application 98101520.9).

According to the present invention, such materials can be brought in an appropriate shape and be used for the production of security elements that can be employed for the production of security papers and other security articles. The security element can have a variety of shapes, for example, but not only, fibre, thread, rod, tape, film and/or combinations thereof. Further, security elements in more complex shapes can be used, for example, but not only, logos, letters, figures, numbers, etc. A significant characteristic for a security article according to the present invention is that the security element comprises at least one photoluminescent segment which is characterised by a linearly polarised photoluminescence or that the security element comprises at least one segment

which is characterised by a linearly polarised absorption, and that the security element is embedded in the security article.

In case of photoluminescent segments, it can be advantageous if normal daylight does not or only weakly lead to the excitation of the luminescent material. In contrast, according to a preferred embodiment of the present invention, it can be advantageous if an additional light source is employed that emits, for example, in the UV, in order to stimulate the photoluminescence of the segment. The linearly polarised photoluminescence of such segments leads to the situation that the emitted light is absorbed by an external polarizer (analyzer) more or less strongly, depending on the orientation of the polar axis of the polarizer (analyzer) and the polar axis of the segment. This, for example, in the case of inspection with the naked eye (and through a polarizer/analyzer), can lead to a strong bright/dark contrast. Of course, this effect can also be detected with suitable sensors. The linearly polarised absorption of such segments, in similar fashion, leads to the situation that linearly polarised excitation light which, for example, can be generated by an external light source in combination with a linear polarizer, is absorbed unequally strong by the segment; depending on the orientation of the polar axis of the excitation light and the polar axis of the segment. The term segment is used for a part of an object, in particular of a security element, for which the characteristic degree of polarization and polar axis for absorption and emission can be determined in appropriate manner. It is obvious to the one skilled in the art that the shape and the size of these segments can vary from case to case and that the measurement of absorption and emission polarization can be performed with a variety of experimental set-ups, for example conventional spectrometers, microscopic methods, etc. If, for example, a fibre based on the some photoluminescent material of a diameter of 0.5 mm and a length of 20 cm that is formed into a circle is considered to be a combination of many segments, because polarization measurements exhibit a strong positional dependence. Of course, also this element exhibits optical effects, analogous to the ones described above and according to the present invention, which can be described by a combination of individual segments.

Dyes:

The security elements in security articles according to the present invention comprise one or more luminescent dyes in suitable concentration and of suitable properties, i.e. which cause the polarization characteristics according to the present invention. Usually dyes only have anisotropic polarisation characteristics in absorption or emission if also the underlying chromophore is structurally anisotropic. Suitable luminescent dyes can, for example, be found in European Patent Applications 97111229.7 and 98101520.9 and in the patent applications and publications cited therein.

Furthermore, the following dyes can be used: 1,4-Bis(5-phenyl-2-oxazolyl)benzene (POPOP, Fluka 15150), 4,4'-Bis(2-benzoxazolyl)stilbene (Uvitex OB ONE, Aldrich

368590), Pergasol Flavin 7G (available also under the trade name Pergasol Gelb GA from Ciba Speciality Chemicals or under the trade name Solophenylflavin 7 GFF; C I Direct yellow 96), Tinopal ABP liquid (particularly suitable for cellulose based elements and for elements based on polar synthetic carrier, also available under the trade name Blankophor P, Bayer, Leverkusen; C I fluorescent brightener 220), , Oxonol 595 (Aldrich 44052-3), Keystone Fluorescent Yellow 10G (available through Keystone Aniline Corp, Chicago, IL 606112). Additionally, a number of azo-dyes such as Congo Red and Sudan Red B are particularly suitable for the described effect in absorbance. The choice of these dyes for particular carrier materials for the security elements can be made by the person skilled in the art based on the usual consideration of the compatibility/polarity of the dye and the carrier. Generally, additional suitable dyes can for example be found in the field of laser dyes and dyes for fluoroimmunoassays.

Other suitable luminescent dyes can be found among optical brighteners as used in textile or paper industry. Many optical brighteners have polarisation characteristics as requested according to the present invention and can therefore be used for dying the security elements. Possible products are for example Blankophor (R) P (liquid), which is a derivative of 4,4'-Diamino-stilbene-2,2'-disulfonic acid (available from Bayer, Leverkusen). This optical brightener gives blue fluorescent effects and is particularly suited for dying elements based on cellulose, namely lyocell, rayon or viscose threads, fibres, etc and those based on polar synthetic polymers such as aramide, polyamide, polyvinyl alcohol and the like. Another suitable optical brightener is Uvitex OB-One, which is a 4,4'-bis(benzoxazol-2yl)stilbene (available from Ciba Speciality Chemicals). This optical brightener also gives blue fluorescent effects after excitation in the ultraviolet range and is particularly useful for dying elements based on a less polar polymer carrier (polypropylene, polyethylene etc.).

Other suitable dyes are generally given by stilbene based textile dyes or other textile dyes. The stilbene unit leads to the anisotropic absorption or emission properties due to its anisotropic geometry. Of course, also other dyes used in textile industry with an anisotropic chromophore not based on the stilbene-unit can be advantageously used. One particular dye used in textile industry which is particularly useful for dying security elements based on cellulose, namely lyocell, rayon or viscose, is available under the name Pergasol Gelb 8 GA, which is a stilbene-dye (available from Ciba Speciality Chemicals). Also this dye can be excited in the ultraviolet range leading to emission of yellow radiation. Absorption as well as emission can be polarised.

Other suitable dyes are inorganic transition metal-ion dyes which also have polarised absorption and/or emission properties.

Of course, also mixtures of the above-mentioned dyes can be used.

Generally speaking, care has to be taken that the material does not have some surface layer/coating which disturbs or even annihilates the polarisation effects when a dye is incorporated/embedded/adsorbed or which prevents or hampers oriented

embedding/adsorption. In particular in the case of fibres, and even more particularly in the field of textile fibres, final coatings are quite common, and these may have to be washed off prior to the dying process. For example in case of textile fibres, the so-called avivage should preferably be removed if the used material interferes with the desired orientation effect. Also, these layers may contain brighteners, colorants and other additives which can have the same detrimental effect as the brighteners and additives possibly present in the matrix of the security article.

Carrier material for the security elements:

As mentioned above, the carrier material carrying the dye must allow an incorporation of the dye leading to a macroscopic polarisation effect, which can be observed by the naked eye or by a particular detector. Usually this requires that the carrier allows an oriented incorporation/embedding of the dye which in turn means that it should usually have some structural orientational order which may be achieved by stretching for example. This high orientational order is measurable e.g. by wide-angle x-ray diffraction, where the order should be characteriseable by a half width at half height of less than 20 degrees, preferably of less than 15 degrees, and even more preferably of less than 10 or even 7 degrees. Another possible mechanism allowing for oriented adsorption of the dye on the surface of the security carrier may be a particularly orientationally structured surface of said carrier.

Polymer based carrier material:

Among the polymer materials suitable in the context of the present invention and also generally for producing elements with polarised emission or absorption are the following:

According to a particular embodiment, the carrier polymer allows for the fabrication of blends comprising at least one PL dye and at least one carrier polymer by melt-mixing, which can be shaped by melt-processing. Production of the polymer carrier can however also be carried out by different methods like solution casting or spinning.

We have found that semicrystalline polyolefins such as polyethylene polypropylene, for example, are useful as carrier polymer in preferred embodiments of the present invention. For example, we have found that if for example linear low-density polyethylene (LLDPE) is used as a carrier polymer, security elements can be manufactured, according to the present invention, that exhibit unusually high dichroic ratios in absorption. Other examples of semicrystalline or amorphous polymers that are preferably used as carrier polymer in preferred embodiments of the present invention, are polyvinylidene halides, polyesters, and polyamides, polyacrylonitriles, polyvinylalcohols, aramides, polycarbonates and so forth, and mixtures thereof. In the context of the present invention, also copolymers can be used as the carrier polymer, for example ethylene/propylene copolymers and so forth. The molecular weight of the carrier polymer employed may vary within wide limits.

Polymers having lower molecular weights have, as a rule, good melt processing characteristics. At the other hand, it is well known in the art, that the maximal achievable draw ratio usually increases with molecular weight. As another rule, linear polymers are used by preference on account of their high degree of orientability. The one skilled in the art should be deemed capable of selecting the right carrier polymer, depending on the envisaged application and the dye employed. The orientation within the polymer can e.g. be achieved by drawing after or during the production process of the fibres/threads. Usually, the dye can be incorporated into these fibres either prior to drawing or after, and the dye can either be introduced into the fibre by a diffusion or a solution process.

E.g., oriented polypropylene (e.g. isotactic polypropylene, Polysciences; polypropylene Fina 3374; REO Flock&Faser, e.g. rohweiss, 5mm, 17dtex), polyvinyl-alcohol (e.g. Aldrich 36, 315-4 98-99 %, Mw 85000-146000), aramide fibres or threads are being used in lengths of between 0.5 to 20 mm, preferably of 1 to 5 mm, at 1 to 50 dtex, preferably at between 5 and 20 dtex.

Cellulose based carrier material:

Also possible as material for the carrier of the security elements are cellulose based structures with suitable orientation. These include among others cellophane, lyocell, viscose, rayon etc. Viscose threads with lengths between 1 to 10 mm at 2 to 20 dtex are suitable. In particular products like Bocell (Akzo Nobel), Fortisan (CERMAV), Tencel fibre and cut (CERMAV), Flax, Ramie, viscose polymeric (all CERMAV). In particular certain Bocell, Fortisan, and Tencel fibres show high orientation and were found to be suitable for the present applications.

Particularly suitable are also lyocell-fibres/threads as manufactured by Lenzing . These are available under the trade name Lenzing-Lyocell and show a high degree of orientation at little fibrillation and little crumpling. These fibres can be easily dyed leading to polarised absorption and/or polarised emission of the adsorbed/incorporated dyes and can therefore be used not only for the incorporation into the security articles according to the present invention but also for many other applications. These other applications may for example be in the field of cloth, textiles, garments, woven and non-woven labels, films, credit cards, etc.

Generally in the context of fibres (synthetical or natural) it has to be pointed out that possible coatings interfering with the present polarisation effects should preferably be removed, that the fibres should preferably be transparent in the visible range, and that the fibres should be free from defects and distortions such as kinks as much as possible. Preferentially, if kinks are present, the straight segments should be longer than the typical length for the detection of the polarisation effect. So in case of observation by the naked eye, which usually allows a resolution of about 10 μm, the majority of the straight segments should preferably be longer than this unit. If this is not the case, the bright/dark effect may not be readily recognised by the naked eye.

For the incorporation into a paper matrix like for example into a banknote, such fibres should be highly oriented (wide-angle x-ray scattering have width at half height of less than 10 degrees), should have a clean, i.e. smooth surface, should be free from defects and kinks i.e. should be straight, should have a length between 3 to 5 mm and a thickness in the range of 10 to 40 dtex, preferably of in the range of 17 dtex. It is also possible to mix natural carriers with polymeric substances as mentioned above and to extrude them together into their final form of a thread, rod, tape, film, etc.

The dyed security elements may be treated after the dying process by methods like embossing and/or by bleaching out certain regions using high-energy a radiation destroying the chromophores in these regions (so-called patterning).

Surface treatment of the security elements:

In order to allow better embedding/fixing of the security elements in the security article/paper, in particular the surface of polymer based fibres/threads or also the surface of polymer coated natural raw material based elements can be modified. Of course, cellulose based fibres usually do not need this surface treatment as for example for the embedding of such fibres into common cellulose-based paper hydrogen bonding possibilities are inherently available in this carrier. Principally this is sometimes necessary to allow a better interaction (e.g. via hydrogen bonds) between the surface of the fibre/thread and the surrounding matrix of the security article/paper. Possible methods of modification are fluorination (carried out in the liquid or in the gas phase), etching with sodiumnaphthalinate (immersion in a solution) or plasma-surface modification and the like. These methods aim at introducing mechanical possibilities of attachment of the fibres/threads in the matrix of the security article/paper or at introducing polar groups at the surface in order to allow the formation of hydrogen bonds between the matrix material and the polymer fibre/thread. The effectiveness of the surface treatment can easily be checked by means of the measurement of the contact angle/of the wettability.

Dying of the security elements:

Suitable methods for the preparation of security elements for the application according to the present invention can, for example, be found in European Patent Applications 97111229.7 and 98101520.9 and in the Patent applications and publications cited therein. As will be evident from the following examples, the security elements or segments of such security elements for the application in security articles according to the present invention, can be produced by the anisotropic deformation of ductile mixtures. As mentioned above, the dying can be carried out either prior to the deformation of the security elements to introduce the structural order necessary for the dyed security elements to exhibit polarising properties or the dye can be introduced into or onto the oriented carrier of the security element. Principally, different dying processes are possible, of which the

particularly useful are diffusion based dying processes and solvent based dying processes.

Usually the dye is dissolved in a suitable solvent (the choice of the solvent or mixture of solvents depending on the polarity of the dye and of the fibre/thread to be treated), the fibres are subsequently added and this mixture is then either kept still or stirred and/or heated and/or refluxed for a certain period of time. In case of cellulose based carrier material the fibres/threads may have to be dried for several hours e.g. in vacuo prior to the dying process. After that the fibres/threads are removed (e.g. by using a filter) and washed once or repeatedly with either the same solvent or another solvent. For less polar dyes and polymeric matrices for the security elements solvents like toluene, benzene, N-Methylpyrrolidone, xylene and the like or mixtures of these solvents can be used for the dying processes. For polar dyes and cellulose based matrices water can be used advantageously as the solvent but also other polar solvents are possible.

Another possible dying mechanism can be vapour deposition of the dye.

Care has to be taken when dying the security elements as for certain carrier material and dye-combinations an excess of dye might lead to a weakening of the polarisation effect.

In particular in case of Lyocell Lenzing fibres water can be used and the dying process is preferably carried out that elevated temperatures like above 80 degrees Celsius washing the isolated dyed fibres two to three times using water of about the same temperature. The resulting fibres show a high degree of polarisation in absorption as well as emission and can therefore be used also for other purposes than for incorporating/embedding into security articles/papers as claimed within this application.

<u>Method of incorporating security elements into paper or the like:</u>

The basic concept of the present invention can principally be applied for all prior art security articles and security papers which comprise at least one security element that is comparable with the one disclosed here, apart, of course, from the linearly polarised photoluminescence, absorption or both. For example, security papers can be made, into which one or multiple photoluminescent threads or strips with properties according to the present invention are embedded. If a multitude of such threads or strips are used, they can, according to a preferred embodiment of the present invention, also exhibit different emission colours and can be arranged in certain patterns, for example, with a specific arrangement of their polar axis'. In another preferred embodiment of the present invention, the security elements are integrated into the substrate in the form of fibres. Also in this latter embodiment the use of security elements with different emission colours can be advantageous, and the fibres can exhibit different shapes; for example, they can be straight or curled, which leads to different optical effects.

Paper fibres:

The fibres which can be used in the present context are synthetic fibres as well as natural raw material based fibres. In case of natural raw material based fibres e.g. wood- based-fibres (chemical wood pulp), cotton-fibres, grass-fibres, cellulose-fibres, viscose-fibres, lyocell-fibres, rayon-fibres, and mixtures of these fibres can be used. It has to be noted that also these fibres usually show some degree of orientation and might influence the polarisation effects of the security elements to be embedded within the paper-like matrix. Therefore a careful choice as well as a carefully chosen amount of these fibres has to be found for an optimum effect.

The fibres are preferably milled to a length in the range of 0.4 to 4 mm, preferably to a length of in the range of 0.6 to 1.2 mm.

Filler:

A number of fillers can be used for the paper-like structure to carry the security element. Usually fillers are added due to their low price, and to produce certain properties like opacity, stiffness, printing properties etc. E.g. titanium dioxide either in its rutile or in its anatase modification as well as zinc oxide can be used, as well as zinc sulphide, lithopone (zinc sulphide and barium sulfate), caoline, silicates, carbonates and the like. To enhance the particular polarisation effects or rather not to disturb the polarising effects due to the security elements, the filler can be chosen such as to absorb as much of the incident polarised or not polarised radiation as possible. For example the use of titanium dioxide in its rutile or at anatase modification as well as zinc sulphide prove to be particularly useful. In particular when rutile is used as filler or at least added to the filler in a sufficient amount of usually 1 to 2 % (this percentage, as mentioned above, sometimes preferentially being higher in case of the additional presence of certain resins, brighteners and the like in the matrix), the paper-like structure appears completely dark when irradiated with ultraviolet irradiation which means that the incident light is completely absorbed by this filler. It is also possible to incorporate organic or other inorganic ultraviolet absorbers into the matrix to achieve the same results, i.e. to eliminate all irradiated ultraviolet irradiation which is not harvested by a particular fibre. This leads to two effects which are particularly advantageous in this context:

First of all, almost no incident light reaches security elements which are buried under a layer of paper-matrix thus avoiding that these buried elements are irradiated by light which is not highly polarised in case of polarised excitation. When polarised light is used for polarised excitation, polarisation gets partially or fully lost when this light passes through layers of the matrix carrying the security element. Correspondingly, light emitted by buried security elements is also not highly polarised anymore leading to a masking of the wanted bright/dark effect when for example rotating the polarisation axis of the incident light. The same is of course true if the incident light is not polarised but if detection is carried out using a polarisation filter. In this case the linearly polarised

photoluminescence emitted by the security elements which are buried is also reduced in its polarisation when passing through the layer covering the buried security element leading to a masking or even to a loss of the bright/dark effect. Surprisingly, it has been observed, that if rutile (or to a lesser degree also anatase or zinc oxide) is being used as filler or at least sufficiently added to the filler, this effect can be avoided. It is due to the high scattering effects of the rutile particles and/or due to the absorption properties of these particles. The particularly high refractive index of rutile (which is higher than for the anatas-modification) is quite well known. However, that this leads to the advantageous effects in the context of the present application of embedding security elements is surprising finding. Even more so as the particle size of the titanium dioxide in rutile-modification does not seem to have the determining influence in this question. Additionally, the highly symmetric structure of the unit cell of the rutile structure leads to fully isotropic properties when polarised light is irradiated.

Another advantage of using rutile as filler is due to the black appearance of the paper-like structure when irradiated with light thus increasing the contrast between the paper matrix and the security elements.

As mentioned above, the amount of e.g. rutile effectively necessary to achieve the above effect may depend on other substances possibly present in the matrix. These are substances which themselves have fluorescent effects in the sense that they absorb ultraviolet light and subsequently emit visible light leading to a bright appearance of the matrix. Usually 1 to 2% w/w of rutile are sufficient to provide the requested ultraviolet-dullness.

Generally, optimal effects are achieved if when irradiating ultraviolet light of about 365nm at an excitation bandwidth of about +/-15nm and excitation power of 15 mW/cm2 in the bandwidth region, using a photomultiplier voltage of 800 V and a measuring slit of 2 mm, on the unprinted paper, the counts per second in the visible range are below 40 between 400 and 450 nm, below 40 to 15 in the range of 450 to 550 nm and below 15 between 550 and 700 nm. This criterion can be used to adjust the content of e.g. rutile-filler.

Additionally, the desired black appearance of the paper-like structure when irradiated with light thus increasing the contrast between the paper matrix and the security elements can be achieved very efficiently by the incorporation of organic substances commonly known as 'uv-absorbers' into or onto the paper matrix. Such substances can typically be found among the classes of benzophenones, benzotriazenes and benzotriazoles and are, eg., commercialised by Ciba Speciality Chemicals under the trade names 'Tinuvin' and 'Chimassorb'. Furthermore, any other organic substance capable of undergoing the transition known to be responsible for the uv absorbing properties in the above-mentioned classes of uv absorbers (known to the one skilled in the art as 'excited state intramolecular proton transfer', or 'ESIPT') are suitable. Additionally, any other substance showing considerable absorbance in the wavelength regime of interest can be considered suitable, such as common dyes and stains, eg. azo-derivatives or polymethin-derivatives.

Other components of the paper-matrix:

The paper-matrix may contain other additives like e.g. binder, colorants, resins, surfactants, detergents, anti-foaming agents, etc which may be necessary in the production process of for particular properties of the paper matrix. These additional components are however minor components. Their possible influence on the general appearance of the paper matrix when irradiated with ultraviolet light or other light used for the excitation of the dye incorporated in the security elements has been discussed above.

Paper production process:

If the security article shall be a paper or paper-like article, it can be produced according to standard paper production technology. However, if dyed fibres have to be incorporated, these fibres should be added to the pulp just prior to starting the actual paper production process, i.e. after the milling process, in order to minimise introduction of defects into the security elements. Also possible is the incorporation of security elements in the form of threads according to the present invention by using a process as described in EP 59056.

Examples:

Example 1: Dying of polypropylene-fibres

50 litres of toluene (xylene also possible but slightly less effective) and 25g of brightener (Uvitex OB-One, available through Ciba Speciality Chemicals or as 4,4'-Bis(2-benzxazolyl)-stilbene available from Aldrich, No. 36,859-8) are heated to 45 degrees Celsius, then 5 kg of polypropylene-fibres (polypropylene-fibres, REO Flock&Faser, length: 3 mm,17 dtex) are being added and the mixture is left at 45 degrees Celsius for 24 hours. The fibres can then be taken out of the bath and do not have to be rinsed prior to their incorporation into a paper or paper-like structure.

Generally, it is observed that the dying process should be carried out in case of polypropylene-fibres above 40 degrees Celsius, i.e. typically in arranged between 40 to 50 degrees Celsius. Usually rinsing does not seem to be necessary.

Example 2: Dying of lyocell/viscose fibres

100 litres of water, 500 ml of brightener (Blankophor P, liquid) and 3.7 kg of fibres (Lenzing Lyocell, length: 2.5 mm, 17 dtex; or length: 4 mm, 6.7 dtex) are being mixed and heated up to 90 degrees Celsius. The mixture is stirred and kept at this temperature for 30 minutes, the fibres are then taken out and allowed to drip off the solution. The fibres are then added to 100 litres of water at 90 degrees Celsius and stirred for 15 minutes. Again the fibres are taken out and allowed to drip off the water. This rinsing procedure is

repeated at least once. Subsequently, the fibres are being centrifuged and dried at about 50 degrees Celsius. If some coating is present on the surface of such fibres it can be removed by washing it away in hot water prior to the dying process. Possible avivage is eliminated in the present process by carrying out the dying process in water and preferably at elevated temperature.

Example 3: Dying of lyocell/viscose fibres

100 litres of water, 10g of dye (Pergasolgelb 8GA) and 3.7 kg of fibres (Lenzing Lyocell, length: 2.5 mm, 17 dtex; or length: 4 mm, 6.7 dtex) are being mixed and heated up to 90 degrees Celsius. The mixture is stirred and kept at this temperature for 30 minutes. Subsequently the colorant is fixed on the fibres by adding 1 kg NaCl to the solution and stirring. The fibres are then added to 100 litres of water at 90 degrees Celsius and stirred for 15 minutes. Again the fibres are taken out and allowed to drip off the water. Subsequently, the fibres are being centrifuged and dried at about 50 degrees Celsius.

Concerning examples 2 and 3 the dying process improves for temperatures above 80 degrees Celsius and should be carried out at 90 to 95 degrees Celsius. The rinsing process should also be carried out at elevated temperature of at least 80 to 90 degrees Celsius, and in the case of the brightener should be repeated at least twice.

Example 4: Dying of polypropylene-fibres with POPOP

20 mg of POPOP (1,4-Bis(5-phenyl-2-oxazolyl)-benzene, Fluka 15150) are dissolved in 5 ml chloroform. 10 mg polypropylene fibres (REO Flock&Faser) are added. The mixture is kept for 2 h at a temperature of 80 °C. The fibres are subsequently removed from the solution, washed with chloroform and dried at ambient temperature. The obtained fibres show the described effect with medium contrast in fluorescence.

Example 5: Dying of uniaxially oriented polypropylene films with Uvitex OB ONE

Uniaxially oriented poly(propylene) sheets (Nowofol) are kept for 2 h in a saturated solution of Uvitex OB ONE (Aldrich 368590) in chloroform for 2 h. The sheets are subsequently removed, washed with chloroform and dried at ambient. The obtained blend films exhibit the described effect with high contrast in fluorescence.

Example 6: Production of Poly(propylene)films with Uvitex OB ONE by melt-processing techniques

Poly(propylene) (i-PP Fina 3374, pellets) is blended with 0.05% w/w Uvitex OB ONE (Aldrich 368590) in a twin-screw extruder at a temperature of 180 °C. The polymer/dye

blend is extruded and melt-processed into a foil. Subsequent uniaxial tensile deformation of stripes of this film at 130 °C yields a product with the described effect with high contrast in fluorescence.

Example 7: Dying of Viscose fibres with Tinopal ABP liquid

660 mg of Tinopal ABP liquid (Ciba special chemicals) are mixed with 110 ml water and heated to 80 °C. A bundle of viscose fibres (Fortisan, Akzo) are immersed in the solution and the mixture is kept for 30 min. The bundle is subsequently removed from the solution, thoroughly washed with water and dried at ambient. The obtained blend films exhibit the described effect with good contrast in fluorescence.

Example 8: Production of Poly(propylene)films with Keystone Yellow 10G by melt-processing techniques

Poly(propylene) (i-PP Fina 3374) is blended with 0.5% w/w (Keystone Yellow 10G, Keystone Aniline Corp., Chicago; K Y 10G) in a twin-screw extruder at a temperature of 180 °C. The extruded polymer/dye blend is melt-processed into a foil. Subsequent uniaxial tensile deformation of stripes from that foil at 130 °C yields a product exhibiting the described effect with recognisable contrast in fluorescence.

Example 9: Production of Poly(ethylene) films with Keystone Yellow 10G and Uvitex OB One

Poly(ethylene) (LLDPE, Dowlex 2340) is blended with 0.5% w/w (Keystone Yellow 10G, Keystone Anliline Corp., Chicago ; K Y 10G) and 0.05% w/w Uvitex OB ONE (Uvi, Aldrich 368590) in a twin-screw extruder at a temperature of 180 °C. The extruded polymer/dye blend is melt-processed into a foil. Subsequent uniaxial tensile deformation of stripes from that foil at 130 °C yields a product exhibiting the described effect with good contrast in fluorescence.

Example 10: Dying of viscose fibres with Congo Red

20 mg of Congo Red (Aldrich 860956) are dissolved in 50 ml water. The solution is heated to 80 °C. A bundle of viscose fibres (Bocell, Akzo) are added and kept for 10 min. The bundle is subsequently removed from the solution, washed with water and dried at ambient. The obtained fibres exhibit the described effect with high contrast in absorbance (colourless to red).

Example 11: Dying of viscose fibres with Oxonol 595

20 mg of Oxonol 595 (Aldrich 44052-3) are dissolved in 50 ml water. The solution is heated to 80 °C. A bundle of viscose fibres (Bocell, Akzo) are added and kept for 10 min. The bundle is subsequently removed from the solution, washed with water and dried at ambient. The obtained fibres exhibit the described effect with good contrast in absorbance (colourless to blue) as well as with recognisable contrast in photoluminescence (dark to dull red).

Example 12: Production of Poly(vinylalcohol) / Congo Red blend film

4 g Poly(vinylalcohol) (Aldrich 36,315-4) is dissolved in 196 ml boiling water to make a 2% w/w solution which is subsequently allowed to cool to room temperature. A base solution of Congo Red (Aldrich 860956) is produced by dissolving 20 mg of the dye in 50 ml water. 1 ml of this solution is stirred into 10 g of the poly(vinylalcohol) solution and casted into a petri dish. After evaporation of the solvent at ambient, a homogeneously coloured blend film is obtained. Stretching of strips of that film at temperatures up to 180 °C yields a thread exhibiting the described effect with high contrast in absorbance (colourless to red) when observed through a rotating optical polariser.

The quality of the dyed security elements according to example is 1 to12 shall be summarised as follows:

Example No	Matrix	Dye(s)	Effect	Production method	Quality
1	PP fibres	Uvitex OB One	PL	Diffusion dying	++
2	Viscose fibres	Blankophor P	PL	Direct dying	++
3	Viscose fibres	Pergasolgelb 8GA	PL/Abs	Direct dying	++
4	PP fibres	POPOP	PL	Diffusion dying	++
5	PP film uniaxially	Uvitex OB ONE	PL	Diffusion dying	+++
6	PP	Uvitex OB ONE	PL	Melt processing	+++
7	Viscose fibres	Tinopal ABP liq	PL	Direct dying	++
8	PP	K Y 10G	PL	Melt processing	+
9	LLDPE	Uvi/K Y 10 G	PL	Melt processing	++
10	Viscose fibres	Congo Red	Abs	Direct dying	+++
11	Viscose fibres	Oxonol 595	Abs/PL	Direct dying	++
12	PVA	Congo Red	Abs	Solution casting	+++

The fibres according to examples 1 to 4,7, and 10 to 11 can be incorporated into paper using standard paper production technique. Three particular examples shall be given:

Example 13:

1600 kg of fibre (cotton-fibre) are mixed with 20 m3 of water. 28 kg of silicate (SiO_2, Zeolex, Martifin-Werke), 14 kg of titanium dioxide (anatase, Titanweiss A1002), 0.4 kg of colorant (Gelb Ocker), 5 kg of titanium dioxide (rutile, Bayertitan RU) and mixed with 3 kg carboxymethylcellusose (Tylose R 1500). This mixtures is milled through several cycles to achieve an average length of fibre of 0.7 to 1.1 mm at a milling degree of 55 to 65 SR. Only now the dyed fibres are added and the pulp is filled up with water to a solid content of approximately 0.5% to 1%. This pulp is then used in a standard paper production process using a cylinder mould machine or a foudrinier technique. The paper produced has a basis weight of approx. 60 to 120 g/m2. The paper shows pronounced bright/dark effect of the incorporated fibres.

Example 14:

20 m^3 of water, 12 kg of starch, 12 kg of titanium dioxide (rutile, Bayertitan RU), 1000 kg of cellulose fibres (chemical wood pulp), 250 kg of cotton fibres and 30 kg of silicate (SiO_2, Zeolex, Martifin-Werke) are mixed. Subsequently, 25 l of aluminasulphate-solution as well as 200 l of caoline-solution are added and the mixture is milled in several cycles to a milling degree of approx. 25 - 45 SR. Only now the dyed fibres are added and the pulp is filled up with water to a solid content of approximately 0.5% to 1%. This pulp is then used in a standard paper production process using a cylinder mould machine or a foudrinier technique. The paper produced has a basis weight of 30 up to 320 g/m^2, preferably of 60 to 120 g/m^2. The paper shows pronounced bright/dark effect of the incorporated fibres.

Example 15:

A pulp according to one of the example is 13 or 14 or mixtures of these examples is used in a paper production process involving 2 cylinders. One of the cylinder is running with a pulp without dyed fibres while the other one contains dyed fibres. The two webs individually produced by the two cylinders are joined immediately behind the cylinder to form a laminate, one side of which shows the polarisation effects according to the invention, while the other side does not.

Example 16

A pulp according to one of the examples 13 or 14 or mixtures of these examples is used in a paper production process involving 3 cylinders. The three webs individually produced by the three cylinders are joined or couched immediately behind the cylinder to form a laminate, the top and the bottom side shows the polarisation effects according to the invention, while the centre ply does not.

Example 17

On a laminating machine, two or three or more layers of produced paper according to one of the examples 13 to 16 are laminated or pasted together. These separate webs, individually produced are joined and pasted or glued together to get an individual laminate of paper or board with a basis weight range of approx. 80 - 700 g/m². The top and the bottom layer show the polarisation effects according to the invention, while the centre ply does not.

Example 18

The Paper and board qualities of example 15 - 16 - 17 can also be created whilst one of the middle layer shows the polarisation effects according to the invention, and not the top or bottom layer. This can be a special hidden security feature.

CLAIMS

1. Security article characterised by at least one security element comprising at least one photoluminescent segment which is characterised by a linearly polarised photoluminescence and/or linearly polarised absorption,

   characterised in that

   the photoluminescent segment is at least partially embedded in a paper or paper-like structure composed of 30 to 99 percent in dry weight fibres and 70 to 1 percent in dry weight filler and optionally additives, complementing to 100 percent in total.

2. Security article according to claim 1, characterised in that the paper or paper-like structure is substantially free of brightener and/or additives which itself have fluorescent properties in particular which itself show linearly polarised photoluminescence and/or linearly polarised absorption.

3. Security article according to claim 2, characterised in that the paper or paper-like structure is substantially free of stilbene-based brightener and/or additives.

4. Security article according to one of the preceding claims, characterised in that the filler has high scattering properties and/or high absorption properties in the spectral range used for irradiation and/or detection.

5. Security article according to claim 4, characterised in that the filler contains or is substantially composed of titanium dioxide in its anatase-modification or composed of zinc oxide or particularly of titanium dioxide in its rutile-modification.

6. Security article according to claim 5, characterised in that 0.5 to 5%, preferably 1 to 2 % of the filler is titanium dioxide in its rutile-modification.

7. Security article according to claim 4, characterised in that the absorption properties in the filler at least partially arise due to one or more organic substances, wherein these organic substances are preferentially chosen in the group of azo-derivatives, benzophenones, benzotriazoles, polymethin-derivatives or benzotriazenes or mixtures thereof.

8. Security article according to one of the preceding claims, characterised in that the fibres at least partially comprise synthetic-fibres selected from the group of polyethylene-fibres, polypropylene-fibres, aramide-fibres, polyamide-fibres, polyacrylonitrile-fibres and/or in that the fibres at least partially comprise natural raw material based fibres selected from the group of wood-fibres, cotton-fibres, grass-fibres, cellulose-fibres, viscose-fibres, lyocell-fibres, rayon-fibres.

9. Security article according to one of the preceding claims, characterised in that at least one of the security segment is characterised by linearly polarised absorption.

10. Security article according to one of the preceding claims, characterised in that said security segment is characterised by a dichroic ratio of 2 or more in absorption and/or emission, preferably of 5 or more in absorption and/or emission, and even more preferably by dichroic ratio of 10 or more in absorption and/or emission.

11. Security article according to one of the preceding claims, characterised in that said security segment has a shape selected from the group consisting of fibre, thread, rod or a combination thereof.

12. Security article according to one of the preceding claims, characterised in that said security segment can be excited to photoluminesce through exposure to electromagnetic irradiation of a wavelength between 200 and 500 nm.

13. Security article according to one of the preceding claims, characterised in that said security segment is made of a polymer carrier, preferably made of polyethylene, polypropylene, polycarbonate, polyvinyl alcohol, or aramide dyed with a photoluminescent dye.

14. Security article according to one of the claims 1 to 11, characterised in that said security segment is made of a cellulose-based carrier dyed with a photoluminescent dye.

15. Security article according to claim 14, characterised in that said security segment is made of a viscose-fibre, or a lyocell-fibre with a length of 0.5 to 25 mm, preferably of 1.0 to 5 mm at 1 to 40 dtex, preferably at 5 to 20 dtex.

16. Security article according to one of the preceding claims, characterised in that the paper or paper-like structure is composed of 70 to 97 percent in dry weight paper-fibres and 30 to 3 percent in dry weight filler and optionally additives, complementing to 100 percent in total.

17. Application of the security article according to one of the preceding claims for objects the forgery of which shall be made difficult or impossible.

18. Application of the security article according to claims 1 - 16 for objects the authenticity and/or validity of which shall be marked.

19. Application of the security article according to claims 1 - 16 for objects the identification of which shall be enabled and/or facilitated.

20. Application of the security article according to claims 1 - 16 for an object selected from the group consisting of banknotes, checks, stocks, bonds, identification cards, passports, drivers licenses, tickets, stamps, bank cards and credit cards.

21. Process for the production of a security article according to claims 1 - 16, characterised in that at least one security segment is dyed with a photoluminescent dye prior or after its structural internal orientation, and is then embedded in a paper-like matrix.

22. Process according to claim 21, characterised in that the fibres are added to the pulp just prior to the actual paper production process.

INTERNATIONAL SEARCH REPORT

International Application No
PCT 01/13588

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 D21H21/48 //D21H17:67

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 D21H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAPERCHEM

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 00 19016 A (ETHZ INST FUER POLYMERE ;SMITH PAUL (CH); WEDER CHRISTOPH (CH)) 6 April 2000 (2000-04-06) cited in the application the whole document	1,17-22
A		8-13

Y	US 6 035 914 A (KLATT LEON N ET AL) 14 March 2000 (2000-03-14) the whole document	1,17-22
A		9,11,13

Y	WO 00 00697 A (PLASCHKA REINHARD ;BURCHARD THEO (DE); GIESECKE & DEVRIENT GMBH (D) 6 January 2000 (2000-01-06) page 3, line 3 - line 7; example 1	1,17-22
A		8,16-20

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
5 June 2002	02. 08. 02

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Nestby, K

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International Application No
PC _ 01/13588

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	GB 2 300 596 A (PORTALS LTD) 13 November 1996 (1996-11-13) page 5 -page 6; figure 1; examples 1,2	1,17-20
A		4,5,8,16

Y	GB 2 299 036 A (COATED PAPERS LIMITED) 25 September 1996 (1996-09-25) page 1 -page 4; claims 13-15	1,17-20
A		4,5,8,16

INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP 01/13588

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1, 4-22

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claims: 1,4-22

   Security article with security element comprising photoluminescent segment embedded in a paper or paper-like structure composed of fibres and filler and optionally additives.

   Application of the security article and process for the production of a security article.

2. Claims: 1-3,8-22

   Security article with security element comprising photoluminescent segment embedded in a paper or paper-like structure composed of fibres and filler and optionally additives, but said paper or paper-like structure is substantially free of brightener and/or additives which itself/themselves has/have fluorescent properties.

   Application of the security article and process for the production of a security article.

INTERNATIONAL SEARCH REPORT

International Application No
PC 01/13588

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			EP	1115949 A1	18-07-2001
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			AU	4779099 A	17-01-2000
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			WO	0000697 A1	06-01-2000
			EP	1099024 A1	16-05-2001
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GB 2299036	A	25-09-1996	NONE		